

## Method for growing oxide thin films containing barium and strontium

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5 The present invention relates to high permittivity oxide films and superconductive materials which contain barium and/or strontium. A particular object of the invention is the method according to the preamble of Claim 1 for producing such films and materials.

10 Dielectric thin films having high dielectric constants (permittivities) are required in many sub-areas of microelectronics and optoelectronics. In particular, the continual decrease in the size of microelectronics components has increased the need for the use of such dielectric films. For example, the capacitance of DRAM (Dynamic Random Access Memory) capacitors must remain nearly constant while their size decreases rapidly, and thus it is necessary to replace the previously used  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  with materials which have higher permittivities than these. In optoelectronics, dielectric films having high permittivities can be exploited in, for example, electroluminescence displays, in which the operating voltage of the displays can be reduced by means thereof. Some dielectric materials having high permittivities, e.g.  $\text{BaTiO}_3$ , are also ferroelectric materials at normal temperatures, a factor which further extends their potential uses, for example, to NVRAM (Nonvolatile Random Access Memory) and various microelectromechanical applications.

20 In addition to high permittivities, these dielectric thin films are required to have, among other things, low leakage current densities and high dielectric breakdown fields. The achievement of both of these properties presupposes a dense and flawless film structure. Of course, the properties of the films must be stable in the conditions of use. Furthermore, in particular in microelectronics applications, the conformality of the films, i.e. their capacity to cover surfaces of complicated shapes with a film of a uniform thickness is important, because in the manufacture of microelectronics components it is necessary to deposit films even in deep trenches and holes.

30 Oxide thin films containing barium and strontium are widely used and researched dielectric films having high permittivities. Important oxide thin films containing barium and strontium include, for example,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  (x is 0-1). In addition to these there can be mentioned high-temperature superconductors, e.g.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (x is 0-1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ , and dielectric materials lattice-

matched therewith,  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{Sr}_2\text{AlTaO}_6$  (D.L. Schulz and T.J. Marks, *Advanced Materials* 6 (1994) 719). In all of the above-mentioned formulae,  $n$  is 1-3 and  $\delta$  is 0-1. Other oxide films containing barium and strontium include various niobates  $(\text{Sr,Ba})\text{Nb}_2\text{O}_6$  and  $(\text{Pb,Ba})\text{Nb}_2\text{O}_6$  (L.M. Shepard, *Ceramic Bulletin* 71 (1992) 85). These films have been  
 5 manufactured by many different methods, such as the sol-gel method, various physical vapor deposition methods (PVD) (e.g. vaporization, sputtering, laser ablation) and chemical vapor deposition methods (CVD).

Films manufactured by the sol-gel method, by various physical vapor deposition methods  
 10 (PVD) (e.g. vaporization, sputtering, laser ablation) and by chemical vapor deposition methods (CVD) are of a high quality. Instead, the manufacture of a film of uniform quality and thickness when the surface structure of the piece is complicated will not succeed. Only by the CVD method is it possible to deposit conformal films in deep trenches and holes (S.M. Bilodeau, *Solid State Technology*, July (1997) 235). Even in the CVD method, high  
 15 conformality is attained only when the rate of film growth is determined by the rate of the surface reaction and not by the diffusion of the precursors on the film surface. This is achieved when the surface reaction is slower than the diffusion of the precursors on the film surface. The surface reaction is slow at low temperatures, but in such a case the other properties of the film will, however, often remain poor, which is due to both the poor  
 20 crystallinity of the film and to difficulties in the control of its composition (C.S. Kang et al., *Japanese Journal of Applied Physics, Part 1* 36 (1997) 6946; M. Kiyotoshi and K. Eguchi, *Electrochemical Society Proceedings* 97-25 (1997) 1063).

Atomic Layer Epitaxy (ALE), which is also known as Atomic Layer Chemical Vapor  
 25 Deposition (ALCVD) or Atomic Layer Deposition (ALD), is a known method for the deposition of thin films (US patent publication 4.085.430). In this method, the thin film is deposited by means of alternate saturating surface reactions. These reactions are implemented by feeding gaseous or vaporized precursors into the reactor alternately and by purging the reactor with an inert gas between the precursor pulses (T. Suntola, *Thin Solid*  
 30 *Films* 215 (1992) 84; Niinistö et al., *Materials Science and Engineering B* 41 (1996) 23). In addition, ALE can be used for depositing layers of uniform thickness even on large surfaces, and the control of the thickness and composition by means of the number of reaction cycles is precise and simple.

The ALE method has previously been used for making TiO<sub>2</sub> films (Ritala et al., Thin Solid Films 225 (1993) 288, Chemistry of Materials 5 (1993) 1174 and 6 (1994) 556), but so far it has not been possible to manufacture the barium- and strontium-containing oxide thin films which are the object of the present invention by the ALE method in a self-controlling manner. Attempts at self-controlling deposition of superconductive films have also failed. The most important reason for not manufacturing the above-mentioned compounds is the lack of suitable precursors for Ba and Sr. Few of the compounds of the said elements are volatile, and so the precursors used in both CVD and ALE have as a rule been of one compound type, i.e.  $\beta$ -diketonates (W.A. Wojtcak et al., Advances in Organometallic Chemistry 40 (1996) 215, Tiitta and Niinistö, Chemical Vapor Deposition 3 (1997) 167). The problem with the  $\beta$ -diketonates of Ba and Sr is that they do not react with the oxygen sources, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>, most typically used in the ALE method, at temperatures at which they would not decompose thermally. Iodides of the said metals have also been used in the CVD method (P. Mårtensson and A. Hårsta, Journal of Crystal Growth 156 (1995) 67), but in this case it is necessary to use temperatures which are too high for most applications.

EP application publication No. 344 352 describes a method for making laminated superconductors by an epitaxy method. The ALE method is also mentioned. The application publication also lists suitable organometallic compounds which can be used as precursors in these methods. Barium cyclopentadienyl is also among them. However, in the publication a film has not been deposited by specifically the ALE method and by using specifically barium cyclopentadienyl as the precursor. Furthermore, the EP publication does not provide preferred conditions for the film growth, since it does not state how or in what conditions cyclopentadienyl compounds should be used, how oxygen is introduced into the oxides or what advantages would follow specifically from the use of barium cyclopentadienyl as the precursor in any of the alternative epitaxy methods described in the publication.

It is an object of the present invention to eliminate the deficiencies described above and to provide a novel method for the manufacture of thin films and superconductive materials which contain barium and strontium.

The invention is based on the observation that the barium and strontium compounds

according to the invention are sufficiently stable in a gas phase, and consequently these compounds can be used as precursors in the ALE technique, and thus oxide thin films which contain barium and strontium can be deposited in a controlled manner. The cyclopentadienyl compounds of barium and strontium are such vaporizable compounds. In the deposition of film, the said barium and strontium compounds are used as precursors in a method according to the ALE principle together with a reactive oxygen precursor and a volatile titanium compound.

More specifically, the method according to the invention is characterized by what is stated in the characterizing part of Claim 1.

The invention will be discussed below with the help of the accompanying drawings.

Figure 1 depicts the composition of a multi-component film as a function of the cycle ratio of the various components.

Figure 2 depicts an X-ray diffraction analysis of the thin film.

Figure 3 depicts the permittivities of films deposited at 325 °C, as a function of the cycle ratio, as measured from the structure ITO/SrTiO<sub>3</sub>/Al, where ITO is indium-tin oxide.

In the technical solution according to the invention, oxide thin films are deposited in an ALE reactor at a temperature of 100-700 °C, preferably 150-400 °C. Either sheet-form (such as glass or silicon wafer) or pulverous materials can be used as the substrate.

According to the ALE method, a cyclopentadienyl compound containing an earth-alkali metal is vaporized, whereafter the reactor is purged with an inert gas, the oxygen precursor is fed into the reactor, and the reactor is purged for a second time with an inert gas. All of these steps together constitute one deposition cycle. The deposition cycle is repeated until the film is of the desired thickness. A multi-component film is obtained by changing the precursor.

In connection with the present invention, cyclopentadienyl compounds of barium or strontium are used as precursors. By these compounds is meant any compound according to Formulae I-IV.



in which formulae

M is Ba or Sr;

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Cp is a cyclopentadienyl group, the Cp groups present in Formulae I and II being mutually the same or different;

X is a ligand other than Cp, with the valency of -1;

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$L_n$  is a neutral adduct ligand which binds to a metal by either one or several of its atoms, and n depicts the number of the ligands being bound.

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In Formulae I-IV the cyclopentadienyl groups may also be in the same molecule. In this case the bridge between two Cp groups is made up of a substituted or unsubstituted  $C_1-C_6$  chain, which may contain a heteroatom which is Si, N, P, Se or S.

Ligand X is preferably  $\beta$ -diketonate or a corresponding sulfur or nitrogen compound, halide, amide, alkoxide, carboxylate or Schiff base.

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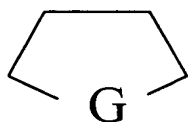
L is preferably

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- (i) a hydrocarbon,
- (ii) an oxygen-containing hydrocarbon,
- (iii) a nitrogen-containing hydrocarbon,
- (iv) a sulfur-containing hydrocarbon,
- (v) a phosphorus-containing hydrocarbon,
- (vi) an arsenic-containing hydrocarbon,
- (vii) a selenium-containing hydrocarbon, and/or
- (viii) a tellurium-containing hydrocarbon.

Most preferably L is

- (a) an amine or a polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



(V)

in which formula G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, cyano or silyl group. The cyclic or aromatic ring of R<sup>1</sup> may contain a heteroatom. The ligand depicted by Formula V may also have either hydrogen or a substituent like R<sup>1</sup> attached to the carbon atoms,

(d) ether or thioether.

The cyclopentadienyl group (Cp) in Formulae I-IV is of the form



where m is an integer of 0-5,

Cp' is a fused or individual cyclopentadienyl, and

R is a hydrocarbon radical containing 1-20 carbon atoms, preferably a C<sub>1</sub>-C<sub>6</sub> hydrocarbon. The R's may be mutually the same or different. R may be a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, amino, cyano or silyl group. The cyclic or aromatic ring of the substituent may contain a heteroatom. Methyl, ethyl, propyl and isopropyl groups can be mentioned as examples of the substituents.

Preferably there is used an organometallic complex according to Formula II, where Cp is cyclopentadienyl, indenyl or fluorenyl. As the neutral adduct ligand L (Formulae II and IV) there are used, for example, ethers, amines or solvent molecules (e.g. tetrahydrofuran) which bind to the metal by one atom. Polyethers and polyamines can be mentioned as examples of suitable ligands which bind to the metal by several of their atoms.

According to the invention, the precursor used for the oxide thin film is especially preferably a THF adduct of bis(pentamethylcyclopentadienyl) or bis(triisopropylcyclopentadienyl) of barium or strontium.

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According to the first preferred embodiment of the invention, the cyclopentadienyl compounds of barium and strontium are used together with a volatile titanium compound (e.g. a halide, alkoxide, cyclopentadienyl, alkylamide) and a reactive oxygen precursor (e.g.  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ), in which case  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  films can be grown by the ALE method at low deposition temperatures ( $325^\circ\text{C}$ ). The said precursors can also be exploited in ALE deposition of other oxide thin films containing barium and/or strontium.

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Below there are listed titanium compounds which have vapor pressures sufficient at a temperature lower than the temperature of the deposition substrate, and which are thus suitable for use in the method according to the present invention. Thus, preferably one or more of the following compounds are used as the volatile titanium compound:

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- titanium halides, for example  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{TiBr}_3$ ,  $\text{TiI}_4$ ,  $\text{TiI}_3$ ,
- titanium alkoxides, for example  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$ ,  $\text{Ti}(\text{O}^n\text{Bu})_4$  and titanium(IV)-ethylhexoxide,
- titanium nitrate ( $\text{Ti}(\text{NO}_3)_4$ ),
- alkylamino complexes of titanium, for example tetrakis(diethylamino)titanium, tetrakis(dimethylamino)titanium, tetrakis(ethylmethylamino)titanium, tetrakis(isopropylmethylamino)titanium, bis(cyclopentadienyl)bis(dimethylamino)titanium, tris(dimethylamino)(N,N,N'-trimethylethyldiamino)titanium, and tert-butyltris(dimethylamino)titanium; further examples of applicable compounds are described in US patent No. 5,659,057,
- cyclopentadienyl complexes of titanium, for example  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2$ ,  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^7\text{-C}_7\text{H}_7)$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{TiR}_2$ , where R = alkyl (e.g.  $\text{CH}_3$ ), benzyl ( $\text{C}_6\text{H}_5$ ) or carbonyl, bis(t-butylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl) titanium dichloride, and  $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ ,
- silylamido complexes of titanium, such as  $\text{Ti}\{\text{N}_4[\text{Si}(\text{CH}_3)_3]_4[\text{Si}(\text{CH}_3)_2]_2\}$ ; further examples of applicable compounds are described in US patent No. 5,603,988,
- titaniumdialkyldithiocarbamates, and
- titanium- $\beta$ -diketonates, for example di(i-propoxide)bis(2,2,6,6-tetramethyl-3,5-

heptanedionato)titanium, and tris(2,2,6,6,-tetramethyl-3,5-heptanedionato)-titanium(III).

Especially preferably, titanium tetraisopropoxide ( $\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$ ) is used.

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The oxygen precursor may be any oxygen compound usable in the ALE technique. Preferable oxygen precursors include water, oxygen and hydrogen peroxide, and aqueous solutions of hydrogen peroxide. Ozone ( $\text{O}_3$ ) is an especially preferable oxygen precursor. It is known on the basis of the literature that, if ozone is used as the precursor for oxygen, a denser layer of material is obtained from the forming oxides, and thereby the permittivity of the oxide thin film can be improved.

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One or more of the following compounds may also be used as the precursor for oxygen:

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- oxides of nitrogen, such as  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_2$ ,
- halide-oxygen compounds, for example chlorine dioxide ( $\text{ClO}_2$ ) and perchloric acid ( $\text{HClO}_4$ ), the compatibility of these with earth-alkali metals being, however, limited,
- peracids ( $-\text{O}-\text{O}-\text{H}$ ), for example perbenzoic acid ( $\text{C}_6\text{H}_5\text{COOOH}$ ) and peracetic acid ( $\text{CH}_3\text{COOOH}$ ),
- alcohols, such as methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), and
- various radicals, for example oxygen radical ( $\text{O}^\cdot$ ) and hydroxyl radical ( $\cdot\text{OH}$ ).

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According to a second preferred embodiment, the ratio of the deposition cycles (e.g. Ti-O, Sr-O and Ba-O) producing the different binary oxides of multicomponent oxide films (e.g.  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ) is controlled. If, for example, Sr/Ti is 0.8-1.2, preferably approx. 1, a crystalline film is obtained (cf. Example 1). Thus the composition can be controlled simply and with precision. In order that the composition of the film should be uniform, the deposition cycles are carried out so that the different materials become mixed as completely as possible, i.e. there will be 1-10, preferably 1-2 similar cycles in succession.

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According to a third preferred embodiment, the oxide film is grown at a lower temperature (250-300 °C), whereby an amorphous thin film is obtained. The structure of the film



becomes crystalline during postannealing. The postannealing is carried out at a temperature higher than the growth temperature, and its duration may vary. According to a preferred embodiment of the invention, the duration of the postannealing is 60 min, and it is carried out in an air stream at 500 °C.

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Considerable advantages are gained with the help of the invention. Since according to the ALE method the film grows through saturating surface reactions, the growth is self-controlling, which in turn ensures excellent conformality. As is evident from the above, cyclopentadienyl compounds of strontium and barium can be used as vaporizing components within a wide temperature range, in which case the structure of the thin film made and its crystallinity can be effectively controlled by the selection of the reaction temperature and the metal mixing ratio and by a potential post-treatment. The present precursors are especially advantageous for use in the ALE technique also for the reason that they will not leave significant carbon or hydrogen residues in the final product. On the other hand, the dielectric constants of oxide thin films containing barium and strontium are very high, and thus the oxides of specifically barium and strontium are especially suitable as materials for dielectric thin films. Owing to their high dielectric constants they are especially suitable for memory circuits and for gate oxides. By the use of cyclopentadienyl compounds of barium together with a volatile titanium compound, a low-temperature growth process is achieved, which is important in most applications of dielectric films.

In the context of the present invention, by dielectric oxide thin film is meant a thin film having a high permittivity. The permittivity varies according to the thickness of the film so that the permittivity of a thinner film is lower. It can be noted as an example that for a film approx. 50 nm thick a high permittivity is approx. 50 or more, preferably approx. 100 or more.

Thin films according to the invention are preferably used as dielectric films of various electronics components. Films according to the invention are deposited, for example, on platinum (Pt), RuO<sub>2</sub>, IrO<sub>2</sub>, SrRuO<sub>3</sub>, LaSrCoO<sub>3</sub>, IrO<sub>2</sub>/Ir, RuO<sub>2</sub>/Pt, silica (SiO<sub>2</sub>), silicon nitride and silicon surfaces.

By means of the present invention it is possible to make, in addition to the above-mentioned thin films, also high-temperature superconductors mentioned in the preamble,

for example  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x$  is 0-1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$  and  $\text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ , and dielectric materials lattice-matched therewith, such as  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and  $\text{Sr}_2\text{AlTaO}_6$  (D. L. Schulz and T. J. Marks, *Advanced Materials* 6 (1994) 719).

- 5 Three examples are presented below in order to illustrate the invention.

### Example 1

- 10  $\text{SrTiO}_3$  films were grown in a flow-type F-120 ALE reactor (Mikrokemia Oy) at a temperature of 325 °C. The strontium precursor used was the THF adduct of bis(triisopropylcyclopentadienyl) strontium,  $\text{Sr}(\text{C}_5(\text{iC}_3\text{H}_7)_3\text{H}_2)\text{THFG}_p$ , in which  $p = 0-2$  and THF is tetrahydrofuran, and which was vaporized in the reactor by heating it to a temperature of 100 °C. The titanium precursor used was titanium tetraisopropoxide
- 15  $(\text{Ti}(\text{O}(\text{iC}_3\text{H}_7)_4)_4)$ , which was vaporized in the reactor at a temperature of 40 °C. The oxygen source used was water, which was fed into the reactor from outside it. The growth of  $\text{TiO}_2$  from the said precursors has been described previously (Ritala et al., *Chemistry of Materials* 5 (1993) 1174).
- 20 The growth of  $\text{SrTiO}_3$  was implemented by using alternate Ti-O and Sr-O deposition cycles. The Ti-O cycle was made up of four steps: (i) an 0.6 s pulse of  $\text{Ti}(\text{O}(\text{iC}_3\text{H}_7)_4)_4$ , an 0.5 s purge with inert nitrogen gas, (iii) an 0.6 pulse of  $\text{H}_2\text{O}$ , and (iv) an 0.5 s purge with nitrogen gas. Respectively, the composition of the Sr-O cycle was: (i) an 0.6 s pulse of  $\text{Sr}(\text{C}_5(\text{iC}_3\text{H}_7)_3\text{H}_2)\text{HTF}_p$ , (ii) an 0.5 s purge with nitrogen gas, (iii) an 0.5 s pulse of  $\text{H}_2\text{O}$ , and (iv)
- 25 an 0.5 s purge with nitrogen gas. The composition of the film was controlled by the ratio of the Ti-O and Sr-O cycles. The alternation of the Ti-O and Sr-O cycles was implemented so that there were at maximum two similar cycles in succession. For example, the cycle ratio  $\text{Ti-O/Sr-O} = 1:1$  was achieved by repeating the cycling formula  $q[(\text{Ti-O})(\text{Sr-O})]$  and the ratio  $\text{Ti-O/Sr-O} = 3:4$  by means of the formula  $q[(\text{Ti-O})(\text{Sr-O})(\text{Ti-O})(\text{Sr-O})(\text{Ti-O})(\text{Sr-O})(\text{Ti-O})(\text{Sr-O})]$ , in which formulae  $q$  indicates how many times the said cycling was repeated.
- 30 Thus  $q$  determines the thickness of the film.

When the films were grown at a temperature of 325 °C, their composition varied according to the cycle ratio (Figure 1). The linearity of the curve shown in the figure is an indication

that the composition can well be controlled by means of the cycle ratio. Films having Sr/Ti ratios close to 1 were, according to an X-ray diffraction analysis, crystalline  $\text{SrTiO}_3$  (Figure 2). TOF-ERDA (Time-of-Flight Elastic Recoil and Detection Analysis) showed that the films contained carbon and hydrogen residues lower than 0.2 at.%, the other possible impurity residues being so low that they cannot be detected by the method concerned.

Figure 3 shows the effect of the post-treatment on the permittivity of the film. The permittivities of films without post-treatment are at maximum 118, but annealing in air at a temperature of 500 °C for 60 min increases permittivity significantly, the highest values being 180. The postannealing also increased the intensity of X-ray reflections, showing an improved film crystallinity.

### Example 2

The process according to Example 1 was repeated using a growth temperature of 250 °C. The films thus grown were amorphous, but they crystallized when they were heated in air at 500 °C for 60 min.

### Example 3

$\text{BaTiO}_3$  films were grown in the manner described in Example 1, but by using instead of  $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_3\text{H}_2)_2\text{THF}_p$  a THF adduct of bis(pentamethylcyclopentadienyl)barium,  $\text{Ba}(\text{C}_5(\text{CH}_3)_4)\text{THF}_p$ , where  $x = 0-2$ . The deposition temperature was 250 °C. When a deposition cycle ratio of  $(\text{Ti-O})/(\text{Ba-O}) = 6:5$  was used, an amorphous film was obtained. When this film was heated in air at 500 °C for 60 min, it crystallized as  $\text{BaTiO}_3$ , for which a measurement showed a permittivity of 165.